TRANSLATOR'S STATEMENT

Assistant Commissioner for Patents,
Washington, D.C.

Sir:

I, Mifune TAKANO, hereby certify:

That I am thoroughly familiar with the Japanese and English languages;

That I am competent to serve as a translator of Japanese documents into English; and

That the attached document represents a true English translation of Japanese application 2003-035487 filed February 13, 2003.

Signed this 19th day of September, 2006.

Translator Mifune TAKANO

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【Document】 Specification

【Title of the Invention】 LOW-TEMPERATURE CURABLE EPOXY RESIN CURING AGENT AND EPOXY RESIN COMPOSITION

【Patent Claims】

【Claim 1】 An epoxy resin curing agent which comprises a polyamino compound obtained by reaction of aliphatic diamine represented by the formula (1) and styrene and a curing accelerator.

$$H_2N-H_2C-A-CH_2-NH_2 \qquad (1)$$

wherein A is a phenylene group or a cyclohexylene group

【Claim 2】 The epoxy resin curing agent according to Claim 1, wherein said curing accelerator has carboxyl group(s) and/or hydroxyl group(s) within the molecule.

【Claim 3】 The epoxy resin curing agent according to Claim 1, wherein said curing accelerator is salicylic acid.

【Claim 4】 An epoxy resin composition comprising epoxy resin and the epoxy resin curing agent according to Claim 1.

【Claim 5】 An epoxy resin cured product obtained by curing the epoxy resin composition according to Claim 4.

【Detailed Explanation of the Invention】

【0001】

【Technical Field of the Invention】

The present invention relates to a low-temperature curable epoxy resin curing agent comprising a polyamino compound and a curing

accelerator. Specifically, the epoxy resin curing agent is applicable to a curing agent for epoxy resin utilized in extremely wide fields including a field of coating materials such as an electrodeposition paint for motor vehicle, a corrosion-resistant paint for ships, bridges and land and marine iron structures, and an inner surface coating paint for beverage cans; a field of materials for electricity and electronics such as a laminated sheet, a semiconductor sealant, an insulating powdered paint and a coil impregnant used in home electric appliances, communication facilities, a control system for automobiles and aircraft and the like; a field of materials for civil engineering and construction such as a material for quake-resistant reinforcement of bridges, a material for lining, reinforcement and repair of a concrete structure, a flooring material of a building , a lining of water supplying facility and sewerage, a pavior for waste water and permeating water; a field of an adhesive for vehicle and airplane, and a field of composite materials for airplane, industrial materials and sports equipment.

【0002】

【Prior Art】

It has widely been known that an aliphatic amino compound and an alicyclic amino compound are used as a curing agent for epoxy resin or a raw material thereof.

Among the aliphatic amino compounds, an aliphatic diamine represented by the following formula (1) has such features that, when it is used as a raw material of a curing agent, it provides a cured product which can be cured quickly at low temperature and has an excellent

chemical resistance.

On the other hand, however, the diamine represented by the formula (1) easily produces carbamate by absorbing carbon dioxide or water vapor in the atmosphere which causes such defects that the phenomena of whitening or stickiness tends to appear on an epoxy resin cured coating film wherein the diamine is used as a curing agent.

【0003】

$$H_2N-H_2C-A-CH_2-NH_2 \qquad (1)$$

wherein A is a phenylene group or a cyclohexylene group

【0004】

Consequently, as a curing agent for epoxy resin, the diamine represented by the formula (1) is scarcely used as it is without modification. In most cases, they are used after various modifications. Representative methods for modification of diamines include a modification by reaction with a compound having a carboxyl group, a modification by reaction with an epoxy compound, a modification by Mannich reaction with an aldehyde compound and a phenolic compound, a modification by Michael reaction with an acryl compound and the like.

【0005】

Among these various methods for modification, a reaction product of Mannich reaction of an amino compound with an aldehyde compound and a phenolic compound has a feature that its curing speed is high. Among them, a Mannich reaction product of diamine represented by the formula

(1) is widely utilized as an epoxy resin curing agent in the field wherein a low-temperature curability is required exploiting the characteristic of its high curing speed. (See Non-patent Document 1)

【0006】

In general, it is preferable that the viscosity of a curing agent is relatively low from the viewpoint of workability. Since a reaction product of Mannich reaction is a modified product of an amino compound with an aldehyde compound and a phenolic compound, it is possible to obtain a Mannich reaction product having a low viscosity by reducing the reaction mole ratio of the aldehyde compound to the amino compound or by increasing the reaction mole ratio of the phenolic compound to the amino compound. However, a relatively large amount of unreacted phenolic compound remains in a low-viscosity Mannich reaction product obtained by such modification. At present, phenol is generally used as a raw-material phenolic compound of the Mannich reaction product. However, since phenol is designated as a poisonous substance and besides, its mutagenicity is identified, it has come to believe that it is not preferable that unreacted phenol is remained in the Mannich reaction product. Thus, a strong tendency not to use phenol has been developed recently.

【0007】

In order to reduce the amount of unreacted phenol remained in the Mannich reaction product, a method such as increasing the reaction mole ratio of an aldehyde compound to an amino compound or decreasing the reaction mole ratio of a phenolic compound to an amino compound

can be applied. However, the viscosity of a Mannich reaction product obtained by such methods becomes high. When the high-viscosity Mannich reaction product is used as a curing agent or a raw material thereof, it is necessary to dilute the product by adding a solvent in order to improve workability.

Recently, there is a strong tendency not to use solvents in an epoxy resin curing agent for a coating material in order to prevent the global environmental pollution, and it is desired to develop an epoxy resin curing agent which is available in a non-solvent condition.

【0008】

An amino compound obtained by modifying metaxylylenediamine and the like is referred as an epoxy resin curing agent in Patent Document 1 which discloses that said amino compound has relatively low viscosity. However, it is described in the above document that said amino compound, when it is used as an epoxy resin curing agent, has a long pot life at room temperature. Therefore, it is believed that curing reaction would not progress in a condition of low temperature.

【0009】

【Non-patent Document 1】

"New Development Of A Curing Agent For Epoxy Resin"

edited by Hiroshi Kakiuchi, published by CMC Co. Ltd., P88, May 31, 1994

【Patent Document 1】

Japanese Patent Kokai (Laid-open) No. 2002-161076, p3-5,

【0010】

【Problems to be solved by the Invention】

An object of the present invention is to provide an epoxy resin curing agent using an amino compound having a low viscosity, an excellent curability at low temperature and an excellent appearance of a coating film without containing environmental harmful substances such as phenol or solvent as a residual component in said amino compound.

【0011】

【Means for solving the Problems】

As a result of extensive studies, the inventors have found that an epoxy resin composition obtained by using an epoxy resin curing agent comprising a polyamino compound obtained by addition reaction of an aliphatic diamine represented by the formula (1) and styrene and a curing accelerator shows an excellent curability at low temperature and an excellent appearance of a cured coating film, and have accomplished the present invention.

【0012】

That is, the present invention relates to an epoxy resin curing agent which comprises a polyamino compound obtained by reaction of aliphatic diamine represented by the formula (1) and styrene and a curing accelerator.

【0013】

$$H_2N-H_2C-A-CH_2-NH_2 \qquad (1)$$

wherein A is a phenylene group or a cyclohexylene group

【0014】

【Embodiment of the Invention】

Examples of the aliphatic diamine represented by the formula (1) to be used in the present invention include orthoxylylenediamine, metaxylylenediamine, paraxylylenediamine, 1,2-bis (aminomethyl) cyclohexane, 1,3-bis (aminomethyl) cyclohexane, and 1,4-bis (aminomethyl) cyclohexane, among which metaxylylenediamine and 1,3-bis (aminomethyl) cyclohexane are particularly preferable.

【0015】

The polyamino compound of the present invention is a compound obtained by addition reaction of aliphatic diamine represented by the formula (1) and styrene, and comprises a polyamino compound which is a mixture of several addition products having different structures of side-chain groups each other as a main component and, other than said polyamino compound, unreacted aliphatic diamine represented by the formula (1) and the like. The preferable content of the unreacted aliphatic diamine represented by the formula (1) is less than 2% by weight. By limiting the content of unreacted aliphatic diamine under 2% by weight, it is possible to reduce the amount of carbamate or carbonate generated by the epoxy resin composition absorbing carbon dioxide or water vapor in the atmosphere and to inhibit the phenomena of whitening

or stickiness of a coating film and deterioration of the appearance of the coating film.

【0016】

In the present invention it is preferable to use catalysts exhibiting strong basicity for synthesizing the reaction product of aliphatic diamine represented by the formula (1) with styrene. Examples of such catalysts include alkaline metal, alkaline metal amide, alkylated alkaline metal and the like. Among them, alkaline metal amide (represented by the general formula MNRR' wherein M is an alkaline metal, N is nitrogen and R and R' are, each independently, hydrogen or an alkyl group) is preferable and lithium amide ($LiNH_2$) is most preferable.

The liquid reaction product obtained after the reaction contains a reaction product and a strongly basic catalyst.. This catalyst can be filtered after changing it to a readily removable salt thereof by adding acids such as hydrochloric acid, hydrogen chloride gas and acetic acid, alcohols such as methanol and ethanol or water and the like.

【0017】

When 2% by weight or more of the aliphatic diamine represented by the formula (1) is comprised in the polyamino compound to be used in the present invention, it is possible to remove it by well-known methods. Though the methods are not restricted, removal by extraction is easy and preferable. The solvent used for extraction is not limited as long as the aliphatic diamine represented by the formula (1) is easily soluble and the reaction product of MXDA and styrene is not soluble therein. The preferable solvent is water.

【0018】

Curing accelerators to be used in the present invention include amine-type curing accelerators as represented by triethylamine and the like, curing accelerators having hydroxyl groups as represented by phenol or benzyl alcohol, curing accelerators having carboxyl groups as represented by formic acid. Among them, the most preferable one to be used is a curing accelerator having carboxyl group(s) and hydroxyl group(s) within the molecule.

【0019】

It is possible to use a compound having at least two kinds of above-mentioned functional groups within the molecule as represented by triethanolamine and lactic acid. However, it is preferable to use a curing accelerator having hydroxyl group(s) and carboxyl group(s) within the molecule. Among them, salicylic acid is most preferable.

【0020】

Though the amount of the curing accelerator to be added is not limited as long as the property of the epoxy resin curing agent of the present invention is not deteriorated, the preferable content is 1 to 20% by weight, more preferably 4 to 15% by weight based upon the total weight of the polyamino compound and the curing accelerator.

When the content of the curing accelerator is less than 1% by weight, the reaction between the epoxy resin curing agent and epoxy resin does not progress sufficiently under the condition of low temperature. When the content of the curing accelerator is more than 20% by weight, the property of the epoxy resin composition obtained

may be deteriorated.

【0021】

The epoxy resin curing agent of the present invention may be used independently, or may be used as a mixture with other polyamine-type curing agents for epoxy resin. In this case, the mixing ratio of the epoxy resin curing agent of the present invention is generally 20% by weight or more, more preferably 30% by weight or more based upon the total weight of the epoxy resin curing agent of the present invention and other polyamine-type epoxy resin curing agents. When the mixing ratio of the epoxy resin curing agent of the present invention is less than 20% by weight, it is not preferable because the characteristic of the epoxy resin curing agent of the present invention may be deteriorated.

【0022】

The epoxy resin composition of the present invention comprises epoxy resin and the above-mentioned epoxy resin curing agent.

Though the epoxy resin used for an epoxy resin composition of the present invention is not limited as long as it has glycidyl groups which can react with active hydrogen atoms derived from amino groups of the epoxy resin curing agent of the present invention, an epoxy resin comprising bisphenol A type epoxy resin, bisphenol F type epoxy resin or the mixture thereof as a main component can preferably be used.

Further, other additives such as components for modification such as filler and plasticizer, reactive or non-reactive diluents, components for adjusting fluidity such as a thixotropic agent, a pigment, a leveling

agent, a tackifier, an anti-cissing agent, an anti-sag agent, an antifoaming agent, an ultraviolet absorber and a light stabilizer may be added to the epoxy resin composition of the present invention depending on the intended use.

【0023】

The epoxy resin composition of the present invention can be cured by well known methods to obtain an epoxy resin cured product. The curing condition is not limited and it can be selected appropriately depending on the intended use. The epoxy resin composition of the present invention shows excellent curability and excellent appearance on the surface of a coating film when it is cured at low temperature of 0 to 15 ℃ as well as when it is cured at room temperature of 15 to 30 ℃.

【0024】

【Examples】

The present invention will be described in more detail below, referring to Examples which are not intended to limit the scope of the present invention. Evaluation of the property of an epoxy resin coating film was carried out by the following method.

[Evaluation of Property of Epoxy Resin Coating Film]

An epoxy resin composition was coated on a steel plate with a thickness of 200 μm under the conditions of 5℃ and 80% RH.

Appearance:

The appearance of a coating film (gloss, clarity, leveling) after 7 days of curing was evaluated visually. Dryness of a coating film after 16 hours, 1 day, 4 days and 7 days of curing were evaluated by touching

with finger.

Water Resistance:

Water droplets were placed on a coating film after 16 hours, 1 day, 4 days, and 7 days of curing. After leaving 1 day, the condition of the coating film was evaluated visually.

Evaluation:

Evaluation was carried out based on the 4 stages of criteria. ◎;Excellent, ○;good △;fair ×;poor

【0025】

EXAMPLE OF SYNTHESIS 1

817.2g (6.0 mol) of metaxylylenediamine, manufactured by Mitsubishi Gas Chemical Co., Inc., in Japan (hereinafter, "MXDA") and 2.9g (0.13 mol) of lithium amide, a reagent manufactured by Merck Ltd., were charged to a flask having internal volume of 2 L (liter) equipped with an agitator, a thermometer, a nitrogen gas inlet, a dropping funnel and a condenser.

Then, its temperature was raised to 80℃ in a nitrogen gas stream with stirring. After raising the temperature, 625.2g (6.0 mol) of styrene, a special grade reagent, manufactured by Wako Pure Chemical Industries, Ltd., in Japan was added thereto dropwise over 2 hours. After the completion of dropwise addition, its temperature was maintained at 80℃ for 1 hour.

Then, 618.2g of distilled water of 80℃ was added thereto. After stirring for 15 minutes, the reaction liquid was kept still for 5 minutes. The upper layer out of separated 2 layers of the liquid in flask was

removed. The same amount of distilled water of 80℃ as mentioned above was added to the residual and the same operation was carried out again. After repeating the same operation for 7 times, distilled water dissolved in the lower layer was removed by vacuum distillation, whereby 1115.2g of polyamino compound A was obtained.

The content of unreacted MXDA in the polyamino compound A was 0.7% by weight base upon the total weight of the polyamino compound and its viscosity was 66 mPa·s/25℃.

【0026】

EXAMPLE OF SYNTHESIS 2

681.2g (4.0 mol) of isophoronediamine (hereinafter, "IPDA") was charged to a flask similar as the one used in Example of Synthesis 1. Then, its temperature was raised to 80℃ in a nitrogen gas stream with stirring. Keeping the temperature at 80℃, 186.0g (0.5 mol) of bisphenol A type liquid epoxy resin with an epoxy equivalent weight of 186g/eq, manufactured by Japan Epoxy Resins Co., Ltd., brand name; Epicoat 828, (hereinafter, "DGEBA") was added thereto dropwise over 2 hours. After the completion of dropwise addition, its temperature was raised to 100℃ and the reaction was carried out at 100℃ for 2 hours, whereby 860.1g of an addition product of IPDA with DGEBA (polyamino compound B) was obtained. The viscosity of the addition product of IPDA with DGEBA was 2865 mPa·s/25℃ and its active hydrogen equivalent weight was 58.

【0027】

EXAMPLE 1

190g of polyamino compound A obtained by Example of Synthesis 1 was weighed and charged to a glass mayonnaise bottle with the volume of 240 ml. Then, 10g of salicylic acid was added thereto and stirred for 3 hours at a temperature of 60℃, whereby 200g of epoxy resin curing agent A was obtained. The viscosity of the epoxy resin curing agent A was 171 mPa·s/25℃. The epoxy resin curing agent thus obtained was mixed with bisphenol A type liquid epoxy resin with an epoxy equivalent weight of 186g/eq, manufactured by Japan Epoxy Resins Co., Ltd., brand name; Epikote 801, and cured under the conditions of 5℃ and 80% RH to prepare an epoxy resin cured coating film, then evaluation of property was carried out. The result was shown in Table 1.

【0028】

EXAMPLE 2

180g of polyamino compound A obtained by Example of Synthesis 1 was weighed and charged to a glass mayonnaise bottle with the volume of 240 ml. Then, 20g of salicylic acid was added thereto and stirred for 3 hours at a temperature of 60℃, whereby 200g of epoxy resin curing agent B was obtained. The viscosity of the epoxy resin curing agent B was 537 mPa·s/25℃.

The epoxy resin curing agent thus obtained was mixed with bisphenol A type liquid epoxy resin with an epoxy equivalent weight of 186g/eq, manufactured by Japan Epoxy Resins Co., Ltd., brand name; Epikote 801, and cured under the conditions of 5℃ and 80% RH to prepare an epoxy resin cured coating film, then evaluation of property was carried out. The result was shown in Table 1.

【0029】

COMPARATIVE EXAMPLE 1

The polyamino compound A obtained by Example of Synthesis 1 was used as it is as an epoxy resin curing agent C.

The epoxy resin curing agent C was mixed with bisphenol A type liquid epoxy resin with an epoxy equivalent weight of 186g/eq, manufactured by Japan Epoxy Resins Co., Ltd., brand name; Epikote 801, and cured under the conditions of 5℃ and 80% RH to prepare an epoxy resin cured coating film, then evaluation of property was carried out. The result was shown in Table 2.

【0030】

COMPARATIVE EXAMPLE 2

190g of polyamino compound A obtained by Example of Synthesis 1 was weighed and charged to a glass mayonnaise bottle with the volume of 240 ml. Then, 10g of diethanolamine was added thereto and stirred for 3 hours at a temperature of 60℃, whereby 200g of epoxy resin curing agent D was obtained. The viscosity of the epoxy resin curing agent D was 102 mPa·s/25℃.

The epoxy resin curing agent D was mixed with bisphenol A type liquid epoxy resin with an epoxy equivalent weight of 186g/eq, manufactured by Japan Epoxy Resins Co., Ltd., brand name; Epikote 801, and cured under the conditions of 5℃ and 80% RH to prepare an epoxy resin cured coating film, then evaluation of property was carried out. The result was shown in Table 2.

【0031】

COMPARATIVE EXAMPLE 3

170g of polyamino compound B obtained by Example of Synthesis 2 was weighed and charged to a glass mayonnaise bottle with the volume of 240 ml. Then, 10g of salicylic acid and 20g of benzyl alcohol were added thereto and stirred for 3 hours at a temperature of 60℃, whereby 200g of epoxy resin curing agent E was obtained. The viscosity of the epoxy resin curing agent E was 3250 mPa·s/25℃.

The epoxy resin curing agent E was mixed with bisphenol A type liquid epoxy resin with an epoxy equivalent weight of 186g/eq, manufactured by Japan Epoxy Resins Co., Ltd., brand name; Epikote 801, and cured under the conditions of 5℃ and 80% RH to prepare an epoxy resin cured coating film, then evaluation of property was carried out. The result was shown in Table 2.

【0032】

【Table 1】

	Example 1	Example 2
Epoxy resin composition (g)		
Epikote 801	100	100
Epoxy Resin Curing Agent A	50	
Epoxy Resin Curing Agent B		53
Property of a cured coating film		
Appearance		
Gloss	◎	◎
Clarity	◎	◎
Leveling	◎	◎
Dryness (16 hours/1day/4days/7days)	△/◎/◎/◎	○/◎/◎/◎
Water resistance (16 hours/1day/4days/7days)	△/○/◎/◎	○/◎/◎/◎

【0033】

【Table 2】

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Epoxy resin composition (g)			
Epikote 801	100	100	100
Epoxy Resin Curing Agent C	48		
Epoxy Resin Curing Agent D		48	
Epoxy Resin Curing Agent E			32
Property of a cured coating film			
Appearance			
Gloss	◎	◎	△
Clarity	◎	△	△
Leveling	◎	◎	△
Dryness (16 hours/1day/4days/7days)	×/×/◎/◎	×/△/◎/◎	×/○/◎/◎
Water resistance (16 hours/1day/4days/7days)	×/△/◎/◎	×/×/○/◎	×/△/○/○

【0034】

【Effect of the Invention】

As clear from the above Examples, the epoxy resin curing agent of the present invention can achieve a low viscosity without containing environmental harmful substances such as phenol and solvents. In addition, the epoxy resin composition using said epoxy resin curing agent shows an excellent curability at low temperature and it provides a cured coating film having excellent appearance.

【Document】 Document of Abstract

【Abstract】

【Problems】

To provide an epoxy resin curing agent achieve having a low viscosity, excellent curability at low temperature and excellent appearance of coating films without containing environmental harmful substances such as phenol and solvents as a residue in the agent.

【Means for solving the Problems】

An epoxy resin curing agent comprising a polyamino compound obtained by reaction of a particular aliphatic diamine with styrene and a curing accelerator.

【Selected Figure】 None